# Dielectric Relaxation Study of $ZnCl_2$ and $ZnBr_2$ Solutions in Water/DMSO Mixtures

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Dielectric spectra have been measured for the title systems up to 72 GHz at 20 °C with salt concentrations ≤1 mol/l. The results are described by a superposition of Debye terms. Two terms are sufficient for binary water/DMSO mixtures, while two additional lower frequency ones are required when salt is added. The results for both halides differ only little. The relaxation strengths of a term ascribable to ionic complexes and a term ascribable to water/DMSO (2:1) complexes vary in opposing sense, demonstrating the competition between those complexes.

## Introduction

Salt solutions in mixtures of water and dimethylsulfoxide (DMSO) are widely applied systems with interesting biological [1] and physicochemical [2–8] properties. These are due to the solvation of the salts as well as to the structural and dynamical peculiarities which are related to the interaction of the two kinds of solvent molecules, in other words to the interplay of ion-solvent and solvent-solvent interactions. Spectroscopic methods are useful in studying those complex systems. Among them dielectric spectroscopy is a suitable tool to gather structural and dynamical information on the polar constituents of the solution, that is not only on both kinds of solvent molecules but also on polar ionic species which eventually may occur.

Dielectric studies of electrolyte solutions are often impeded by too high a conductivity contribution $\varepsilon_c''(\omega)$ obscuring the relaxational part $\varepsilon''(\omega)$ of the dielectric loss spectrum, which is the contribution of primary interest. This is obtained from the measured spectrum $\varepsilon_{tot}''(\omega)$ as the difference

$$\varepsilon''(\omega) = \varepsilon_{tot}''(\omega) - \varepsilon_c''(\omega) \tag{1}$$

where it is usually assumed that

$$\varepsilon_c''(\omega) = \frac{\kappa}{\varepsilon_0\,\omega}; \tag{2}$$

$\kappa$ is the static conductivity and $\varepsilon_0$ the permittivity of empty space.

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The present paper reports some results found for zinc halides in water/DMSO. These salts have been chosen since in particular $ZnCl_2$ is known to form different ionic species in aqueous and also some non-aqueous solutions, such as

$$Zn^{2+} \rightleftharpoons ZnCl^+ \rightleftharpoons ZnCl_2 \rightleftharpoons ZnCl_4^{2-}, \tag{3}$$

which may moreover involve solvent molecules [9, 10]. It is therefore not unexpected that the conductivity in water/DMSO mixtures is low enough to allow for a reliable separation of the relaxational spectrum, as in the case of various non-aqueous solvents studied previously [11, 12].

## Experimental

The dielectric loss spectrum $\varepsilon_{tot}''(\omega)$ was measured over a broad frequency range between 5 MHz and 72 GHz at 20 °C, using various apparatus. The conductivity $\kappa$, which can be obtained from MHz data according to (2), was additionally determined in the kHz range with an impedance bridge. The respective values did agree to within experimental uncertainty. The viscosity was measured with a capillary viscometer.

The binary water/DMSO solvent was studied over the range $x_{DMSO} \approx 0.1 \ldots 0.7$. For the pure substances; data from the Münster laboratory were already available. In order to avoid too high conductivities with the salt solutions, the mole fraction of DMSO in the water/DMSO solvent mixture was restricted to the range $x_{DMSO} \approx 0.3 \ldots 0.6$ and the salt content to $c_s \leq 1.0$ mol/l.

Chemicals from Fluka were used as obtained.

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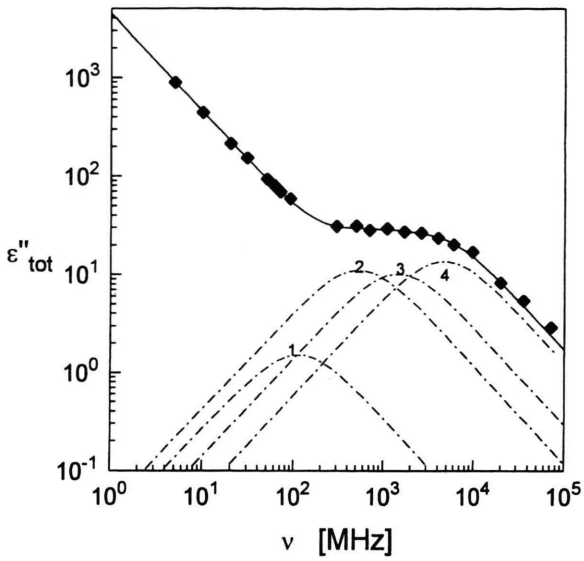


Fig. 1. Dielectric loss spectrum, $\varepsilon''_{tot}$ against frequency $\nu$, for $ZnCl_2$ ($c_s$ = 1.0 mol/l) in water/DMSO ($x_{DMSO}$ = 0.33). Fitting by four Debye type components ($i$ = 1...4) apart of the conductivity contribution.

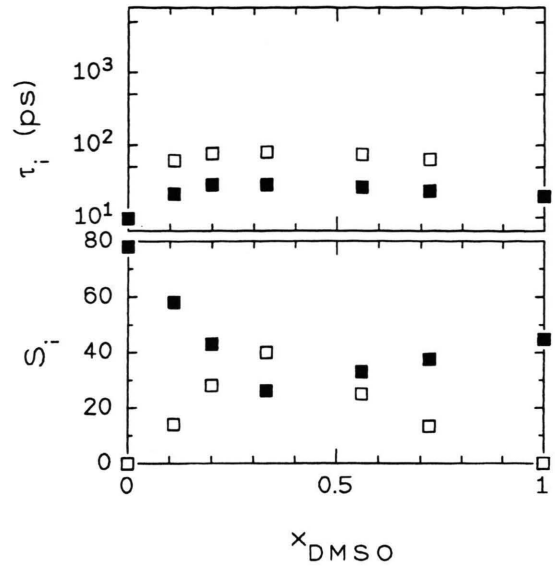


Fig. 2. Relaxation parameters $\tau_i$ and $S_i$ for binary water/DMSO mixtures against DMSO mole fraction $x_{DMSO}$. Symbols for spectral components: □ $C_3$, ■ $C_4$.

## Results

The $\varepsilon''_{tot}$ ($\omega$) data were separated into the conductivity contribution (2) plus a sum of Debye type spectral components $C_i$ describing $\varepsilon''(\omega)$, *viz.*

$$\varepsilon''(\omega) = \sum_i S_i \frac{\tau_i \omega}{1+\tau_i^2 \omega^2} . \qquad (4)$$

The $\varepsilon''$ ($\omega$) spectra of the binary water/DMSO mixtures are clearly broader than a Debye function and can be described by two Debye type components. Instead, Cole-Cole or Cole-Davidson functions have been used in the literature for water/DMSO spectra [13–15]. For the salt solutions, the spectra are further broadened towards the low frequency side. Retaining the two terms found for the solvent in an approximate manner, two additional terms are required to account for that lower frequency broadening. A typical example is shown in Figure 1. Thus four spectral components maximum are used, indexed $i$ = 1 ... 4 in the order of increasing frequency (where $i$ = 3, 4 stand for the components found with the binary solvent mixture).

The fitting parameters, *viz.* relaxation times $\tau_i$ and relaxation strengths $S_i$, are represented in Fig. 2 for the binary solvent mixture and in Figs. 3 and 4 for salt solutions. It may be noted that there are only little differences between the results for $ZnCl_2$ and $ZnBr_2$ solutions.

## Discussion

*Water/DMSO Binary System*

Regarding the relaxation parameters (Fig. 2) in dependence on the mixture composition ($x_{DMSO}$) it is interesting to note that they pass through extrema at $x_{DMSO} \approx$ 0.3. It is well known that interactions between water and DMSO lead to a 'complex' formation DMSO · $2H_2O$, which causes extrema of several physical properties at $x_{DMSO} \approx 0.3$ [13–18].

Qualitatively it is obvious that at least $C_3$ is related to those 'complexes', which may be of transient or long-lived character (relaxation time determined by life-time or reorientation time, respectively). Let it be tentatively assumed that they behave as long-lived, quasi-rigid entities, the relaxation of which is governed by rotational tumbling motion. Then a comparison with the relaxation behaviour of non-associating molecules is possible using the empirical correlation between the relaxation time $\tau$, macroscopic viscosity $\eta$ and effective radius $r_{eff}$ of the tumbling unit, which has been established from a wealth of experimental data [19]:

$$\tau = \tau_0 \left(\frac{\eta}{\eta_0}\right)^{(r_{eff}/r_0)-k_0} , \qquad (5)$$

where the quantities indexed '0' are empirical parameters. For $C_3$, one finds $r_{eff,3} \approx 0.45$ nm, for $C_4$ there is

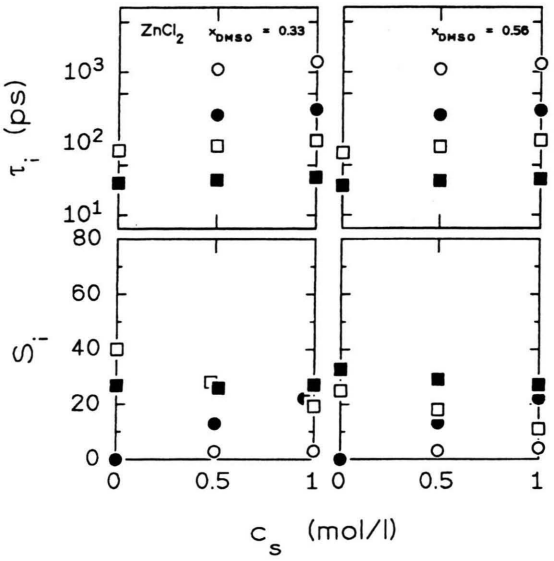


Fig. 3. Relaxation parameters $\tau_i$ and $S_i$ for $ZnCl_2$ solutions against salt concentration $c_s$ for two solvent compositions: $x_{DMSO} = 0.33$ (left) and 0.56 (right). Symbols for spectral components: ○ $C_1$, ● $C_2$, □ $C_3$, ■ $C_4$.

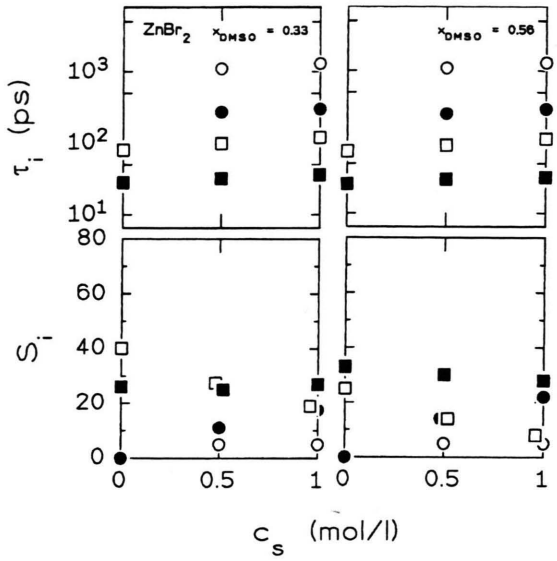


Fig. 4. Same as Fig. 3, but for $ZnBr_2$ solutions.

$r_{eff,4} \approx 0.38$ nm. Usually the correlation (5) allows to estimate $r_{eff}$ from $\tau$ (and $\eta$) to within an uncertainty band of about 0.05 nm. In view of that, the $r_{eff,3,4}$ values do not significantly depend on the mixture ratio and the presence of salt.

The effective radii entering (5) are taken from space filling molecular models. These show that $r_{eff}$ ($H_2O$) ≈ 0.14 nm and $r_{eff}$ (DMSO) ≈ 0.33 nm. The value $r_{eff,3} \approx$ 0.45 nm is not inconsistent with the presumed complex provided an angled configuration. Therefore the relaxation process causing $C_3$ may indeed consist in the tumbling motion of DMSO · $2H_2O$ entities.

For $C_4$, on the other hand, the assumption that relaxation is caused by the tumbling motion of single molecules is unlikely to be tenable since in the case of pure water the relaxation mechanism is governed by association *via* hydrogen bonds, thus being of collective character, and even for pure DMSO there are association-like effects which make (5) inapplicable [19].

*Salt/Water/DMSO Systems*

The spectral components $C_1$ and $C_2$ which appear only in the presence of salt are doubtless related to ionic relaxation processes, while $C_3$ and $C_4$ are ascribable to the solvent as before.

'Ionic' spectral components which closely resemble $C_1$ and $C_2$ inasmuch as they show a similar correlation between their relaxation times and solution viscosity have been observed with a broad variety of electrolyte solutions. It was, however, not found possible to ascribe them in a *general* manner to certain physical relaxation mechanisms [20].

We shall try to discuss the present results in terms of 'chemically' defined species. Unfortunately, the situation is rather complicated even if it is pictured in a minimal fashion. First, concerning conceivable species, one has to take into consideration ion-molecule species (*e.g.* $Zn^{2+}$ with nonsymmetrical, mixed solvation shell, thus acting as polar moiety) and, on the other hand, ion-ion species according to (3) but probably involving solvent molecules [9, 10] (*e.g.* polar solvent shared ion pairs of the $Zn^{2+}(solv)Cl^-$ type). Preliminary results for $Zn(NO_3)_2$ solutions (as well as results for other electrolyte solutions [20]) indicate that $C_2$ might to a considerable degree be related to ion-molecule species, and $C_1$ to ion-ion species. Second, concerning conceivable relaxation mechanisms there are two limiting possibilities, that is the tumbling motion of long-lived species and, on the other hand, the kinetics of the dissociation-association equilibrium in the case of short-lived species.

As already mentioned, the conductivity of the $ZnCl_2$ and $ZnBr_2$ solutions studied is relatively low. This can be seen from the Walden type product $\kappa\,\eta/(z\,c)$, which for $x_{DMSO}$ = 0.33 solutions ranges between 0.008 ($ZnCl_2$) and 0.015

S $cm^2$ $mol^{-1}$ Pa s ($ZnBr_2$). This is less by about an order of magnitude than roughly to be expected for complete dissociation of the salts. In comparison, the corresponding values for $Zn(NO_3)_2$ are in the 0.05 ... 0.08 S $cm^2$ $mol^{-1}$ Pa s range. It seems inprobable that the low conductivity could be accounted for merely by a mobility decrease of solvated $Zn^{2+}$ ions. Therefore ionic complexes according to (3), with reduced or even vanishing charge, should be taken into account in order to interprete the spectral components $C_1$ and $C_2$ of the present salt solutions.

Presupposing the tumbling mechanism, it is worth noting that effective radii estimated for the spectral components $C_1$ and $C_2$ according to (5) are practically independent of solvent composition and salt concentration, $r_{eff,1} \approx 0.60$ nm and $r_{eff,2} \approx 0.51$ nm. From this finding, unsolvated (contact) ion paris can be ruled out. The same would have been concluded from the fact that water and DMSO both act as stronger ligands than the anions $Cl^-$ and $Br^-$.

The most striking finding of the present study is the behaviour of the solvent relaxation strengths $S_3$ and $S_4$ on addition of the Zn salt (Figures 3, 4). While $S_4$ stays nearly unchanged (for $x_{DMSO} \approx 0.3$ even constant), $S_3$ (ascribed to water/DMSO complexes) decreases as $S_2$ (ascribed to ionic complexes) increases. This is strongly indicative of a competition between the two complex types.

In the case of an ion such as $Zn^{2+}$ with filled d-orbital, donor-acceptor properties may play a role apart from purely electrostatic interactions. Since DMSO is a stronger ligand (donor number DN = 29.8) than water (DN ≈ 19), it is probably DMSO which is drawn from the water/DMSO complex to an ionic complex involving solvent. This could be of the ion-molecule type $Zn^{2+}(DMSO)_x(H_2O)_{m-x}$. Depending on the water/DMSO mixture ratio and the salt concentration, preferential solvation by DMSO could occur [21]. Coordination numbers 4, 5, 6 are known for zinc complexes [22]. In aqueous solution the solvation number is usually $m = 6$, but on addition of an organic medium it may decrease to 4, as similarly observed with ions of lanthanoids [23]. Those ions with nonsymmetrical (and mixed) solvation shells might be responsible for the appearance of $C_2$. Conclusions on the character of the underlying relaxation mechanism, however, would be pure conjecture.

At moderate and higher salt concentrations $c_s$, species with an anion $Cl^-$ or $Br^-$ in the outer solvation shell (solvent shared ion pairs) may be formed to a noticeable fraction. Outer sphere complexes of that kind have been found with concentrated aqueous $ZnCl_2$ solutions [9]. These might give rise to the spectral component $C_1$. Although the relaxation strength $S_1$ can be determined only with uncertainty, it seems to increase in a sublinear manner with $c_s$. This might be considered a hint at a subsequent formation of symmetrical, thus nonpolar $ZnCl_2$ or $ZnBr_2$ species.

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